J Therm Anal Calorim (2009) 98:601–607
DOI 10.1007/s10973-009-0511-8

Dynamics of polymeric systems

Empirical formula of temperature dependence of relaxation time

Adam L. Danch

Received: 29 April 2009 / Accepted: 18 September 2009 / Published online: 4 November 2009

Abstract Using dielectric and mechanical relaxation data of polymeric systems, an alternative formula is examined. The formula describes the experimental data with a high degree of accuracy, not received by the other model functions (Arrhenius and non-Arrhenius type) under investigation. The proposed formula gives the answer on questions concerning a supermolecular structure and the nature of the structural relaxation. New definition of the glass-transition temperature is proposed. It is shown how we should combine the results of different experimental methods to conduct an unambiguous analysis of polymeric systems.

Keywords Relaxation time · Polymeric systems · Glass-transition temperature

Introduction

The relaxation spectra of polymers give information on the molecular motion: local and/or cooperative. Various experimental techniques have been established to get knowledge on the molecular dynamics of polymers in the liquid or solid states. The dynamic mechanical (DMTA) and dielectric (DETA) thermal analyses have become a widely used techniques for polymeric material characterisation. The analysis is based on the determination of the temperature dependences of the Young's modulus or dielectric permittivity, respectively [1–3]. The obtained spectra, in both cases, reveal the local and/or cooperative motions which are characterised by their relaxation times. There have been various attempts to explain the temperature dependence of the relaxation time, which often falls with temperature in the thermally activated Arrhenius relationship or the Vogel–Fulcher expression. An alternative approach has been Adam and Gibbs theory, where the molecular dynamics is described in terms of changes in some thermodynamic quantity: a configurational entropy, or the Dolittle free volume approach. A more recent alternative is to apply the dynamic scaling following a power law [4–6].

In general, the following classification of the origin of the relaxation processes in semicrystalline polymers is now accepted [7]:

- motion of small local groups of atoms,
- motion of pendant groups or short side chains,
- motion of fragments (including several mers) of a main chain or cooperative intermolecular motions occurring in unconstrained amorphous regions,
- motion of fragments (including several mers) of a main chain occurring in constrained amorphous regions,
- motion of bulky fragments of polymeric chains associated with premelting.

The temperature dependences of the relaxation times, above-mentioned processes, provide (more or less) a correct fit to the experimental data. The Arrhenius relationship is often invoked to characterised relaxation processes in polymer; although, the activation enthalpy and attempt frequencies are unphysically large in many cases. It is especially characteristic for the relaxation attributed to motions of large fragments of polymeric chains (α relaxation). In this

---

Electronic supplementary material The online version of this article (doi:10.1007/s10973-009-0511-8) contains supplementary material, which is available to authorized users.

A. L. Danch (✉)
Research and Development Center, STOMIX, 79065 Žulová 178, Czech Republic
e-mail: danch@stomix.cz

case, the Vogel–Fulcher or the power expression provides a much improved fit.

The relaxation spectra of polymers reveal the local motions and the cooperative motions in a wide temperature ranges. There is no controversy in the literature concerning the proper description of the former one, for which the Arrhenius expression accurately represents the temperature dependence of the relaxation time. However, the dynamics of the cooperative motions, in particular for highly crystalline polymers without bulky side groups, is disputed. Semicrystalline polymer is capable of being quenched to various levels of crystallinity. Such a treatment causes that the arrangement of chains in the amorphous regions differ, and not only depend on a unit cell type of crystal phase but also on a crystallites location in the polymeric material. Moreover, the constraining effect of the crystallites on the mobility of the chains in the amorphous regions, in some cases, is so strong that the diversity of the amorphous phase can be observed in experiments, e.g. as two separated glass transitions (each of them is represented by the glass-transition temperature, T_g) or two α relaxations (each of them is represented by the characteristic temperature dependence of the relaxation time) [8–10]. The models of supermolecular structures of those systems, i.e. formed by the crystalline domains and two coexisted fractions of the amorphous phase, were proposed for semicrystalline (polyolefines [11]) and liquid crystalline (derivatives of norbornene [12]) polymers. The amorphous phase was divided into the ‘real’ and the ‘ordered’ ones. The ‘real’ one did not exhibit any influence of the constraining effect and the chains behaved as chins in pure amorphous material. The relaxation time (as a function of temperature) was well described by the Vogel–Fulcher expression. The relaxation time of the process occurred in the ‘ordered’ amorphous regions was described by the Arrhenius expression.

The shortcoming of many expressions (models) is that many fitting parameters do not have a straightforward physical meaning and cannot be determined by independent methods [4–6, 13, 14]. Using the concept of double glass transition [8–10], the relaxation processes are analysed for different polymeric systems. The aim of this article is to show that the proposed approach is a generalisation of many applied models, expressing the cooperativity or locality of the motions. The new expression not only fits better experimental data, but also gives information about the mechanism of the relaxations as well as the fitting parameters possess the physical meaning and they can be determined by independent methods. The data analysis is performed for the systems including the coexisted amorphous fractions of various arrangements and new expression, exhibiting the origin of the molecular motions in the α relaxations, is adapted to the temperature dependence of the relaxation time found experimentally.

The formulae descriptions

The relaxation times, deduced from experiments probing the local and/or structural rearrangements in semicrystalline polymers, often fall with temperature in the thermally activated dynamics and the Arrhenius (AR) relationship:

$$\tau = \tau_{\mathrm{AR}} \exp(E_{\mathrm{AR}}/RT) \quad (1)$$

where E_{AR} is the activation energy, τ_{AR}^{-1} is an attempt frequency and R is the gas constant, is used in a fitting procedure of experimental data. Although the AR relationship is often used to interpret data, obtained for structural relaxations (α relaxations) of polymeric systems, the fitting parameters, i.e. E_{AR} and τ_{AR}^{-1} are ridiculously large considering the energy require for polymer decomposition and the highest possible frequency in the material. The Vogel–Fulcher (VF) expression, the most widely used empirical temperature law in the case of the structural relaxation, provides a much better fitting of experimental data. The corresponding expression for relaxation time is:

$$\tau = \tau_{\mathrm{VF}} \exp[B/(T - T_{\mathrm{o}})] \quad (2)$$

with τ_{VF}, B and T_{o} as fitting parameters. In order to modify Eq. 2, one may replace B by DT_{o} and plot $\log(\tau)$ as a function of the reciprocal temperature scaled by T_g (T_g is taken as a temperature at which the relaxation time equals 100 s). D is a dimensionless parameter, which has been called the strength parameter. This modification defined another dimensionless parameter: the fragility, $m = d(log(\tau))/d(T_g/T)$, calculated at $T = T_g$ (T_g is defined as above) [15, 16]. The analysis of data on relaxation times for different systems, performed with using the D parameter, provided the basis for the material classification with two extremes: the ‘strong’ and the ‘fragile’ glass formers. All parameters used in this modification cannot be determined by independent methods. Additionally, the temperature scaling by T_g, taken arbitrary for $\tau = 100$ or 10 s, make this approach incoherent and ambiguous for the data analysis [17, 18]. It is worth noticing that T_{o} is a few tens of degrees below T_g and both the fitting parameters adopt more realistic values than necessary for the AR expression.

It is important to recognise that despite the popularity of the expressions mentioned above many other models have emerged from theoretical study. An alternative approach is the power law [4, 5]:

$$\tau = \tau_{\mathrm{P}}[T/(T - T^*)]^{\alpha} \quad (3)$$

where $\alpha = z\nu$, ν is the critical exponent of the correlation length, z is the dynamic exponent, which treats the relaxation phenomenon in the same way as the critical phenomenon that occurs in the vicinity of a true phase transition at T^*.

More complicated law was obtained based on the Adam and Gibbs theory [19], in which the relevant thermodynamic quantity (configurational entropy, S_c) was used for the expression of the temperature dependence of the relaxation time [4.5]:

$$\tau = \tau_{AG} \exp(C/TS_c) \tag{4}$$

where τ_{AG} is the relaxation time at infinite temperature and C is a constant of an energy dimension.

We can find in literature various attempts to explain the temperature dependence of the molecular dynamics of polymeric systems. The two parameters of Arrhenius law is often a good approximation if relaxation times pointed out in a narrow temperature range are considered. It provides univocal results from statistical point of view, but the values of the fitting parameters, i.e. E_{AR} and τ_{AR}^{-1}, are unphysically large in many cases. However, it was found that the relaxation time of structural relaxation occurred in the 'ordered' amorphous phase is accurately represented by the AR relationship [20, 21]. There is a vast amount of literature on the subject of glass transition, relaxation processes in polymers, and various measurement methods have been developed; however, there are some outstanding questions which still remain to be answer. The basic questions are 'Is there or is there not a true (in the thermodynamic sense) glass transition?' and 'Is there a single relaxation mechanism which governs different relaxations in polymers?'. Another question concerns the relationship between the relaxation process and the glass transition. The mathematical formula of the relaxation time which provides a good fit (in thermodynamic and statistic sense) to experimental data in a wide temperature range is also very important, especially from the material engineering point of view.

Sample preparation and measurements

Results of various experimental methods are used for the characterisation of polymeric material. The analysis is usually based on thermal analysis of a small sample. Every method requires a specific sample preparation to fulfil the method restrictions (technical requirements). The preparations of the samples, investigated by different techniques, very often influence their supermolecular structure [22]. Therefore, in extreme cases, we can investigate the same polymer (the same chemical constitution) but various samples (various supermolecular structures). Owing to the fact that the glass transition and the α relaxation are related to the supermolecular structure, we should apply the samples which have not been influenced by different treatments. Therefore, we should be careful to choose the adequate methods for the complementary study of the polymeric material [20, 21], especially, the semi- or liquid-crystalline one. We may not to compare the measured (estimated) parameters if they are obtained for the samples of different thermal treatments. The most spectacular example is a comparison of the T_g values obtained from the calorimetric (DSC) or the dielectric (dynamic mechanical) measurements. DETA (and in some cases DMTA) may give drastically different spectra for the same polymer that is reflected in different temperature dependences of the relaxation times [9, 12, 20, 21]. Owing to the fact that the T_g values, published in literature for the DSC (the mid-point) and DETA ($\tau = 100$ s) methods, are usually obtained for the measurements performed with some heating (cooling) rate or performed in the step isothermal mode, respectively, we should only use the extrapolated to zero heating rate DSC values for any system description. Another question is whether or not we are able to measure the absolute value of C_p with high precision, using the power compensated DSC, that would reveal the thermodynamic state of the polymeric system correctly? Moreover, we ought to give some answer on a question whether the change of configurational entropy (S_c) at T_g estimated by the following formula:

$$S_c = \int_{T_L}^{T_U} \frac{C_p}{T} dT \tag{5}$$

where T_L and T_U mean the temperatures at which the transition begin and finish, respectively, is well estimated taking into account the proposed calculation and measurement procedures [19, 23, 24].

It is worth noticing that the problems related to the volumetric measurements are also important [25–29]. Which volume influence the mobility of the polymeric chains, the specific (V_s) or free (V_F) one? The former one is estimated from the dilatometric measurements (DIL), while the latter one is evaluated from a positron annihilation lifetime spectroscopy (PALS). The importance of the volume factor is a contentious issue. It is circumvented using pressure, P, as an experimental variable, for a V_s alternation maintaining temperature constant. A general relationship [14],

$$\tau = \tau_V \exp(C/TV^{\gamma}) \tag{6}$$

where τ_V, C and γ are fitting constants, is applied for all glass formers. The parameter γ (a material constant) is postulated to provide a measure of the relative importance of V_s as opposed to temperature.

In this article, the origin of the α relaxation and glass transition, as well as, the relationships between the physical parameters, measured by the above-mentioned techniques, are reconsider in the context of the usefulness of these parameters for the description of the proposed temperature dependence of the relaxation times.

The proposed formula

The empirical formula combines the Arrhenius and Vogel–Fulcher relationships for the temperature dependence of the relaxation time [20, 21, 26]:

$$\tau = \tau_{\mathrm{l}} \cdot \exp(\frac{\Delta H_{\alpha}}{\Delta C_{\mathrm{p}}(T_{\mathrm{g}})} \cdot \frac{1}{T}) \tag{7}$$

where

$$\Delta H_{\alpha} = n_{\alpha} \cdot H_{\mathrm{i}} \tag{8}$$

$$H_{\mathrm{i}} = H_{\mathrm{l}} \cdot \exp((\frac{\Delta T^{*}}{T - T_{0}})^{2}) \tag{9}$$

$$n_{\alpha} = n_{\mathrm{l}} \cdot \left(1 - \frac{1}{1 + (T/T_{\mathrm{c}})^{\beta}}\right) \tag{10}$$

The physical meanings of the used parameters are the following: τ_{l}, the relaxation time at high temperature ($T \rightarrow \infty$, in practice, it is the value in a liquid state, below the polymer decomposition); ΔH_{α}, the enthalpy of the process activation; $\Delta C_{\mathrm{p}}(T_{\mathrm{g}})$, the specific heat change occurred in the glass-transition temperature range; n_{α}, number of mers taking part in the process; H_{i}, the enthalpy of intermolecular interaction; $\Delta T^{*} = T_{\mathrm{m}} - T_{\mathrm{t}}$; T_{m}, the melting temperature, and T_{t}, temperature of the transition involving the α relaxation; T_{0}, temperature at which the relaxation starts; T_{c}, temperature at which 50% of the mers is activated for the cooperative motion. It should be emphasised that the β parameter (reflecting the rate of the mers activation) is strictly correlated with the free volume parameter, δ^{*}, which reveal the possible transition (glass liquid, crystal liquid). In the most general case, the case of the 'semi-ordered' amorphous fraction (SAF), there are five fitting parameters. A result of such a fitting would seem to be useless from statistical point of view. However, the parameters used in the formula posses physical meaning and some of them can be measured (determined) by one of the above-mentioned techniques (DIL, PALS, DSC, DETA/DMTA). It causes that only three parameters are fitted. In the case of the 'ordered' amorphous fraction (OAF), there are two fitting parameters. It has been shown previously for $\tau \rightarrow (T)$ of the α relaxation occurred in OAF (it is named the α_{c} relaxation) that the scaling applied for various systems using the $\Delta C_{\mathrm{p}}(T_{\mathrm{g}})$ values will give the same activation enthalpies if the crystal (liquid crystal) phase, coexisted with OAF in the studied system, is the same type. The application of the AR relationship gave quite different values of the activation enthalpies and it was impossible to find any correlation between the supermolecular structures of OAF and the parameters of the $\underline{\alpha}_{\mathrm{c}}$ relaxation. Moreover, the values of the fitting parameter, E_{AR}, were unphysically large in some cases. Although OAF was studied mainly, some preliminary results concerning the 'real' amorphous fraction (RAF) were also presented [20, 21].

Data analysis

In this article, we consider the usefulness of new formula for the structural relaxation (it is named α_{g} relaxation)

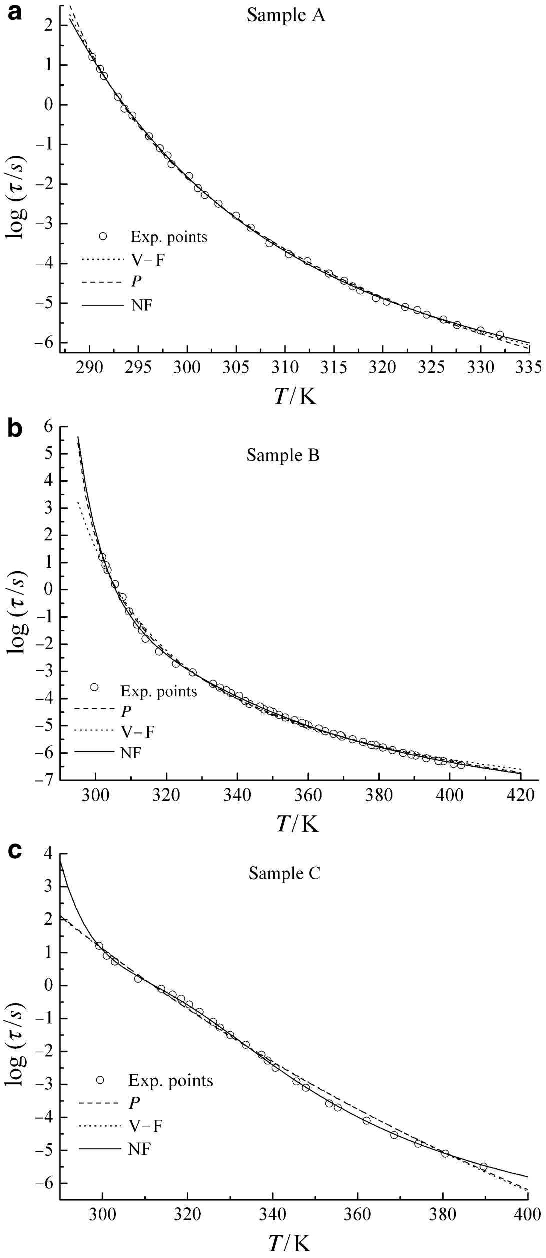

Fig. 1 Activation plot for the relaxation data of liquid crystalline polynorbornene derivative (mechanical and dielectric data taken from literature [13, 16]) including the fits compiled in Table 1: **a** sample A (relaxation of the side chain—smectic structure); **b** sample B (relaxation of the main chain—smectic structure); **c** sample C (relaxation of the main chain—amorphous structure)

occurs only in SAF, focusing on how we should describe the temperature dependence of the relaxation time taking into account the influence of physical processes on the molecular mobility. In polymers, the applicability of the AR relationship is questionable for the α_g relaxation. It is well know that the temperature dependence of Young's modulus (dielectric permittivity in DETA) and consequently the relaxation time are not accurately represented by this relationship. The Fogel–Vulcher (Eq. 2) and power (Eq. 3) expressions provide a much improved fit to experimental data. Figure 1a–c shows plots of $\log(\tau_{\max})$ versus temperature and the curves obtained from the fitting of both the expressions, mentioned above. The figures include also a fit of the new formula. It should be emphasised that each curve seems to give a satisfactory representation of experimental data (DETA and DMTA) and the fitting errors (no weighting χ^2) are rather low. However, the lowest one was obtained in the case of Eq. 7 for each studied example. In order to present the attractions of new expression, three characteristic examples were chosen among the large set of our experimental data for polynorbornene derivative. This complicated system emphasise the advantage of new formula particularly strong. Especially, one can easily find it in Fig. 1c. The VF and P functions slightly depart from the thermal course of τ in the narrow ranges for this case. Moreover, the fitting process generates physically useless parameters (sample C in Table 1). Table 1 presents only three of seven parameters needed for the fitting of the new formula to experimental data. The left parameters, i.e. T_m, T_c, T_t, $n_lH_l/\Delta C_p$, were either fixed (T_m; $T_c = T_g$; T_t; they were taken from the DSC measurements or they were pointed out from the experimental DMTA or DETA data, respectively) or free ($n_lH_l/\Delta C_p$) in the fitting process. In some cases the T_t value was a free parameter; however then, the $\log(\tau_l)$ value had been known from other examples yet. Such a treatment was a result of the assumption that the relaxation time of the α_g relaxation for the polymeric systems built by the same polymeric chains, although they can form various supermolecular structures in the solid state, should be the same for all polymeric systems in a liquid state, for $T \to \infty$. It means that in the most general case only four parameters were assumed to be free in the fitting procedure.

In order to find the T_t values, one should plot the data in a $[d\log(\tau)/d(1/T)]^{-1/2}$ versus $1/T$ representation [5]. The basic idea of such an analysis is to linearise Vogel–Fulcher function and to emphasise deviation between experimental data and the function. Figure 2a–c depicts the data of Fig. 1a–c, respectively, in such a representation, also including the representation of the new function. The inconsistency of the experimental data with the V–F function is seen clearly in Fig. 2b, c. Several V–F functions (each with three free parameters) should be used in the adequate narrow temperature ranges for better fitting in both the cases; however, it increases the number of the fitting parameters. The V–F fits in the linear representation was achieved by a standard linear regression procedure, and the intersection of the adequate straight lines (dotted lines in Fig. 2b, c) marks the range of the functions applicability (T_t). Each of the T_t value was used in the fitting process of the new function; however, only one T_t value gave the lowest χ^2. It is suggested we should considered this T_t value as the most appropriate one for the system description from the dynamics point of view. Table 1 presents in the last column the T_t value used in the fitting. The values obtained from the data linearisation are presented in the figures. One can find that $T_t = T_g$ in the case of the sample A. It would means that the relaxation is completely influenced by the glass transition of the system, being in the pure amorphous state. This conclusion might be deduced from the value of the β parameters ($\beta = 2$) [21, 26]. The phase state of the system was additionally confirmed by X-ray study [12, 30]. The B and C cases required $T_t = 325.9$ K and $T_t = 322.2$ K, respectively. Both the temperatures are the limit temperatures of the activation of the side chains. These are the temperatures (it can be calculated from Eq. 10) at which the side chains are completely activated in the adequate polymeric systems. One

Table 1 Fitting parameters for the curves shown in Fig. 1a–c

Sample	Equation	$\chi^2 \times 10^{-3}$	Log (τ_x/s)	T_o/K	D, α, β	T_g/K	T_t/K
A	VF	1.78	−10.6 ± 0.1	262.3 ± 0.6	1.26 ± 0.04	296.2	296.2
	P	3.36	−14.6 ± 0.2	280.7 ± 0.4	10.7 ± 0.2		
	NF	1.62	−8.9 ± 0.1	126.3 ± 1.1	2		
B	VF	15.87	−9.1 ± 0.2	263.7 ± 1.7	3.35 ± 0.21	312.3	325.9
	P	6.76	−10.9 ± 0.1	292.1 ± 0.5	8.12 ± 0.16		
	NF	2.59	−11.5 ± 0.5	236.9 ± 1.3	14.9 ± 0.9		
C	VF	20.55	−29 ± 5	−0.4 ± 66.2	?	310.0	322.2
	P	20.57	−28 ± 5	17 ± 118	1.1×10^4		
	NF	6.94	−11.5	234.6 ± 0.3	23.0 ± 2.3		

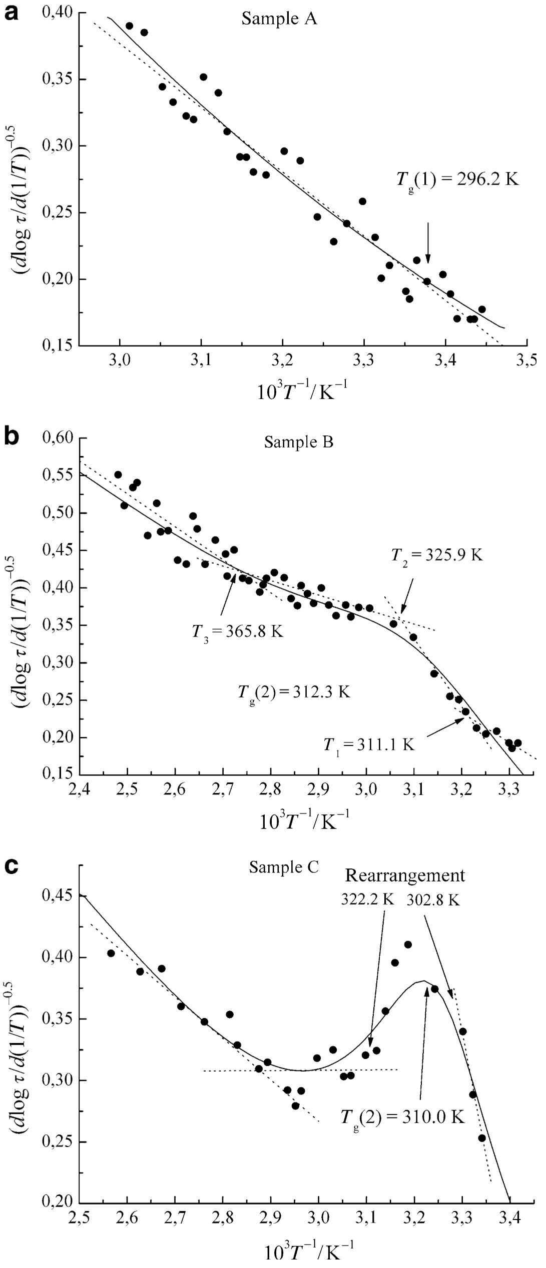

Fig. 2 Data as in Fig. 1a–c in linear representation. The V–F functions are transformed to linear functions (dotted lines): **a** sample A; **b** sample B; **c** sample C, respectively

can conclude that the motion of the large fragments of main chain is possible not before the activation of the whole side chain.

Conclusions

Arrhenius equation has the attraction of having the smallest number of parameters. Vogel–Fulcher equation has been obtained in numerous theoretical treatments of the glass transition. An attraction of the power law is that the fitting generates the parameter (T^*) which might be identified with the T_g value. Owing to these facts, the authors believe that new formula presented here should find general application for detailed comparison of various systems of the same polymer processed in different ways. The new formula should be useful especially to distinguish subtle changes being the result of the inclusion of the secondary phases. The analysis of the chosen samples, representing different polymeric systems, showed that the formula is useful not only for the study of the 'ordered' amorphous phase that was presented in a previous article, but also for the study of the 'semi-ordered' or 'real' amorphous phases using the new formula which gives answer on the basic questions concerning the nature of the glass transition and the α relaxations (α_c, α_g).

Acknowledgements The fruitful discussions with Prof. S. Rzoska (Silesian University, Katowice, Poland), and with Prof. A. Gałęski (Center of Molecular and Macromolecular Studies, PAN, Łódź, Poland) on the constrained amorphous phase in polymeric systems, and the remarks (S.Rz), which helped the author to improve the manuscript, are greatly acknowledged. The opinion written by Prof. R. Hołyst (Inst. Phys. Chem., PAN, Warszawa, Poland) is acknowledged too.

References

1. McGrum NG, Read BE, Williams G. Anelastic and dielectric effects in polymeric solids. New York: Wiley; 1967.
2. Ward IM. Mechanical properties of solid polymers. London: Wiley; 1971.
3. Strobl G. The physics of polymers. Berlin: Springer; 1997.
4. Almond DP, Braddell OG, Harris B. On the analysis of mechanical relaxation at the glass transition in thermoset polymers. Polymer. 1992;33:2234–7.
5. Stickel F, Fisher EW, Richert R. Dynamics of glass-forming liquids I. J Chem Phys. 1995;102:6251–8.
6. Rault J. Origin of the Vogel–Fulcher–Tammann law in glass-forming materials. J Non-cryst Solids. 2000;271:177–217.
7. Volegova IA, Konyukhova EV, Godovsky YuK. Dynamic mechanical characterization of molecular motion in a wide temperature range of various polymers containing propylene units. J Therm Anal Calorim. 2000;59:123–8. (and references therein).
8. Struik LCE. The mechanical and physical ageing of semicrystalline polymers: 1. Polymer. 1987;28:1521–4.
9. Danch A. Dynamic mechanical relaxation in the opaque and transparent PMP films. J Therm Anal. 1998;54:151–9.
10. Danch A, Lohner K, Ungerank M, Stelzer F. Thermal analysis of the conformational disorder in SCLC polymers with rigid backbone. J Therm Anal. 1998;54:161–70.
11. Danch A, Gadomski A. On the crystalline-amorphous supermolecular structure of PMP films cast from solution: experimental evidences and theoretical remarks. J Mol Liq. 2000;86:249–57.
12. Danch A. Structure-dynamic relationship of side-chain liquid crystal polymer with rigid backbone. J Therm Anal Calorim. 1999;56:1097–9.
13. Ngai KL, Roland CM. Development of cooperativity in the local segmental dynamics of PVA: synergy of thermodynamics and intermolecular coupling. Polymer. 2002;43:567–73.

14. Cassalini R, Roland CM. Thermodynamical scaling of the glass transition dynamics. Phys Rev E. 2004;69:062501–3.
15. Angell CA. Formation of glass from liquids and biopolymers. Science. 1995;267:1924–35.
16. Angell CA, Green JL, Ito K, Lucas P, Richards BE. Glassformer fragilities and landscape excitation profiles by simple calorimetric and theoretical methods. J Therm Anal Calorim. 1999;57: 717–36.
17. Hodge IM. Strong and fragile liquids—a brief critique. J Non-cryst Solids. 1996;202:164–9.
18. Mohanty U, Craig N, Fourkas JT. Relationship between dynamical and equilibrium characteristics of glass-forming polymeric liquids. Phys Rev E. 2001;64:010501–3.
19. Adam G, Gibbs JH. On the temperature dependence of cooperative relaxation properties in glass-forming liquids. J Chem Phys. 1965;43:139–46.
20. Danch A, Osoba W. Effect of supermolecular structure on transport phenomenon in polymeric membranes. Desalination. 2004;163:143–53.
21. Danch A. Thermodynamics and structure of the ordered amorphous phase in polymer. J Therm Anal Calorim. 2005;79: 205–8.
22. Danch A, Osoba W. Stability of supermolecular structure below T_g—a role of free and specific volumes in local relaxations. J Therm Anal Calorim. 2006;84:331–7.
23. Alba-Simionesco C, Fan J, Angell CA. Thermodynamic aspects of the glass transition phenomenon II. J Chem Phys. 1999;110: 5262–72.
24. Johari GP. An equilibrium supercooled liquid's entropy in the Kauzmann and the third law exploration and a proposed experimental resolution. J Chem Phys. 2000;113:751–61.
25. Rane S, Gujrati PD. Importance of interactions for free-volume and-group effects in polymers: An equilibrium lattice investigation. Phys Rev E. 2001;64:011801–9.
26. Danch A. On the influence of the supermolecular structure on structural relaxation in the glass transition zone: *free volume approach*. Fibre Text East Eur. 2003;11:128–31.
27. Cangialosi D, Wuebbenhorst M, Schut H, van Veen A, Picken SJ. Dynamics of polycarbonate far below the glass transition temperature. Phys Rev B. 2004;69:134206–9.
28. Danch A, Osoba W. Stability of supermolecular structure below T_g—a role of free and specific volumes in local relaxations. J Therm Anal Calorim. 2006;84:79–83.
29. Cohen MH, Grest GH. Liquid-glass transition, a free-volume approach. Phys Rev B. 1979;20:1077–98.
30. Danch A, Laggner P, Degovics G, Sęk D, Stelzer F. Thermodynamic and structure investigation of new side-chain liquid crystal polymer. In: Tykarska M, Dąbrowski R, Zieliński J, editors. Liquid crystals: chemistry and structure. Singapore: Academic Press; 1998. p. 271–5.